A MASS SPECTROMETER FOR ISOTOPE ANALYSIS

by

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BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

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(B.A., Bryn Mawr College, 1946)

submitted in partial fulfilment of the

requirements for the degree of

Master of Arts

1949

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I. INTRODUCTION

One of the most important applications of physics to
the biological sciences in recent years has been the use of
isotopes as tracers in studies of metabolism, in the location
of diseased cells, and other matters of biological interest.
The general concept of tracer work is startling in its
simplicity, however the execution is often difficult and
tedious. Stated in very general terms, the problem is to in-
troduce a "labelled" element (i.e., an isotope of an element)
into a living organism and to observe how the organism makes
use of the element. This is possible because living matter is
unable to distinguish chemically between the isotope and the
element as found in its natural state, and hence uses both in
the same manner. It is possible, however, to distinguish
between them physically, in all cases due to the differences in
masses, and in many cases due to the fact that a stable element
will have a radioactive isotope. It has been up to the
physicists to devise some means of detecting, quantitatively,
to a high degree of accuracy, the amount of any isotope present
in samples which the biochemist obtains from the living
organism.

The detection of the radioactive isotopes is compara-
tively simple, and requires less complicated equipment than the
stable isotopes. Since the element to be investigated exists

ordinarily in a stable state, any amount in this state will not interfere with the tracer. The matter of detection of the tracer is merely a question of determining the number of dis-intergrations per unit time thrown off by the sample. The most familiar method used is the Geiger-Mueller counter, which amplifies each impulse made by a radiated particle into an electric impulse which operates a counting device. The quantity of the isotope present in a sample will be propor-tional to the number of disintergrations per second emanating from it for a given element. The ionization chamber, the electrometer, and radioautographs are also used in a somewhat similar fashion for radioisotope detection.

Although this method is convenient and practical, it is impossible in certain cases such as the detection of hydrogen, nitrogen, or oxygen, as these elements, which are so important to the living organism, have no radioactive isotopes with use-ful decay periods. The stable isotopes are measured by means of a mass spectrometer. This instrument makes use of the difference of masses of the two isotopes. The instrument ionizes the atoms and molecules in the sample and shoots them through a magnetic field. Since they are charged particles they are deflected by the field, the lighter particles being bent more than the heavier ones. The two isotopes are separated in this manner and are deposited on different collecting plates. The tiny electron current made by the in-dividual ions striking the collector plates is amplified

hugely and so a precise measurement of the ratio of the tracer isotope to the usual isotope of the element may be made.

There have been several other types of mass spectrometers previous to the Nier instrument. Aston developed one in the early 1920's. Aston's method was an improvement over previous positive ray analysis in that it was the first instrument which focussed all positive ions with the same charge per mass in the same place on the photographic plate rather than spreading them out in a parabola as had been done before. With this instrument Aston confirmed the existence of two neon isotopes.

A second type of mass spectrometer was designed shortly afterwards by Dempster. His instrument differed from Aston's in that the photographic plate was replaced by an electrical measuring device. It also has a different disposition of the electric and magnetic fields and all positive ions measured had the same energy.

Bainbridge more recently developed a mass spectrometer with a velocity selector so that all the positive ions had the same velocity rather than energy. This instrument was improved upon by Bainbridge and Jordan, and the new spectrometer was said to have a resolving power such such that the separation between the CO ions and the N_2 ions whose masses differ by 1 part in 2500 was evident.[1]

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[1]Semat, Henry, Introduction to Atomic Physics, Farrar and Rinehart, New York 1939, p. 49.

The Nier instrument is the most recent of all and has been perfected to the extent that it is being manufactured commercially by Consolidated and General Electric. The instruments put out by these companies are essentially the same as the one which was built at Harvard and is described in these pages. Since the commercial spectrometers will probably have a wide distribution and will become standard pieces of equipment for many areas of biological research, it is hoped that the following description will be of interest and importance.

Since mass spectrometers have not been available commercially until very recently, it was proposed at the Biophysical Laboratory of the Harvard Medical School to build one in the laboratory. The work was started in July of 1946. The circuits were obtained from Dr. Alfred O. Nier of the University of Minnesota, who designed them and was in the process of construction of the first of this type of instrument when work at Harvard was commenced. The ion source (or electron gun) and the mass spectrometer tube for the Harvard spectrometer were made by Dr. Nier's technicians as it was highly skilled work. The rest of the constructions was done at the Biophysical Laboratory. The work was done under the close supervision of Dr.Arthur K. Solomon by a graduate student Sidney Solloway, a skilled radio technician Frank Rennie, and the author -- a laboratory technician. After the first year of construction when the instrument was operating but not perfected, the graduate student left and the group was joined
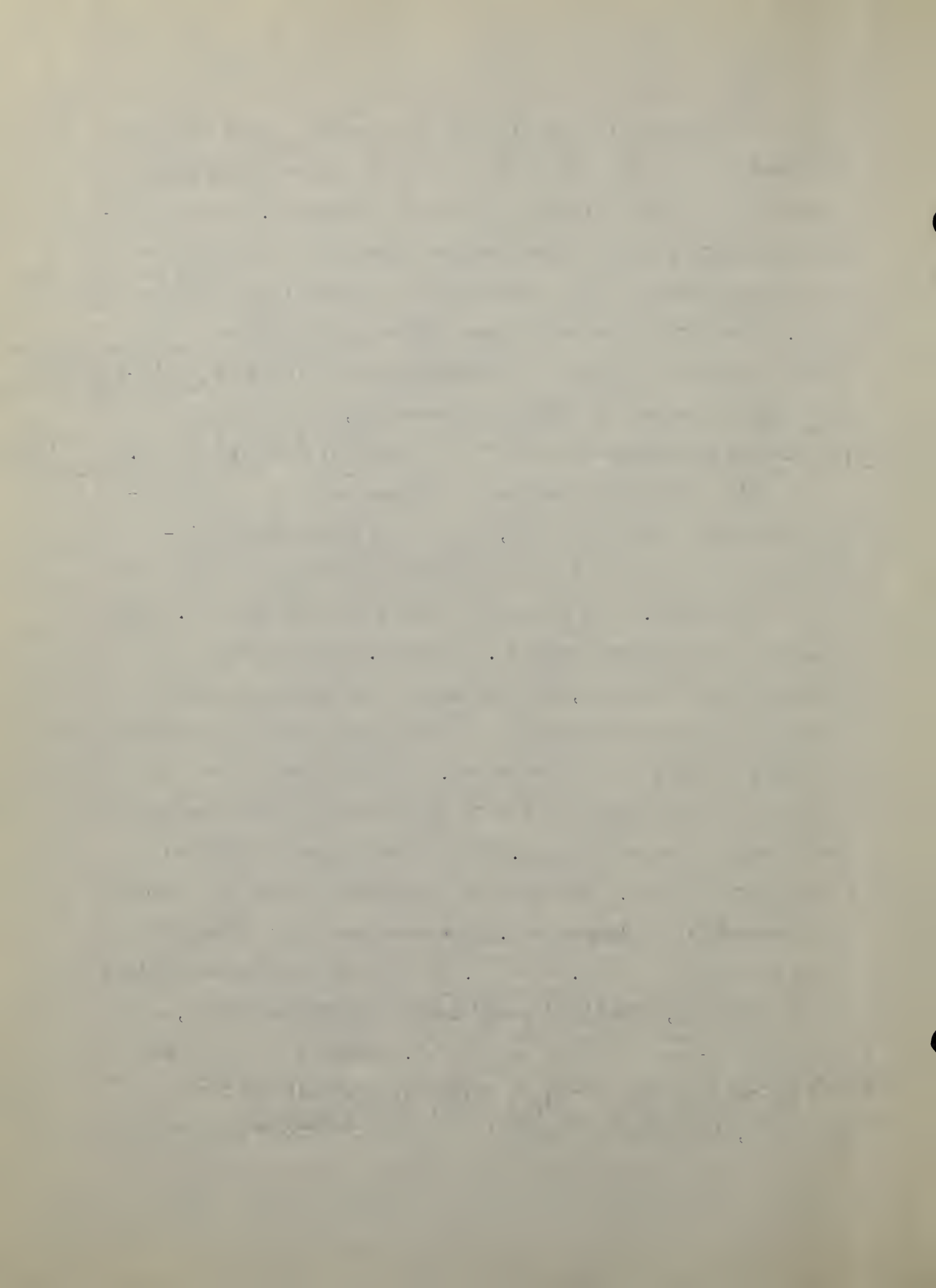
by another laboratory technician, Mary Smythe. This paper
proposes to cover the aspects of construction in which the
author participated during the period from January 1947 through
July 1948.

II. GENERAL DESCRIPTION OF THE NIER TYPE
SPECTROMETER

In order to understand the detailed workings of the
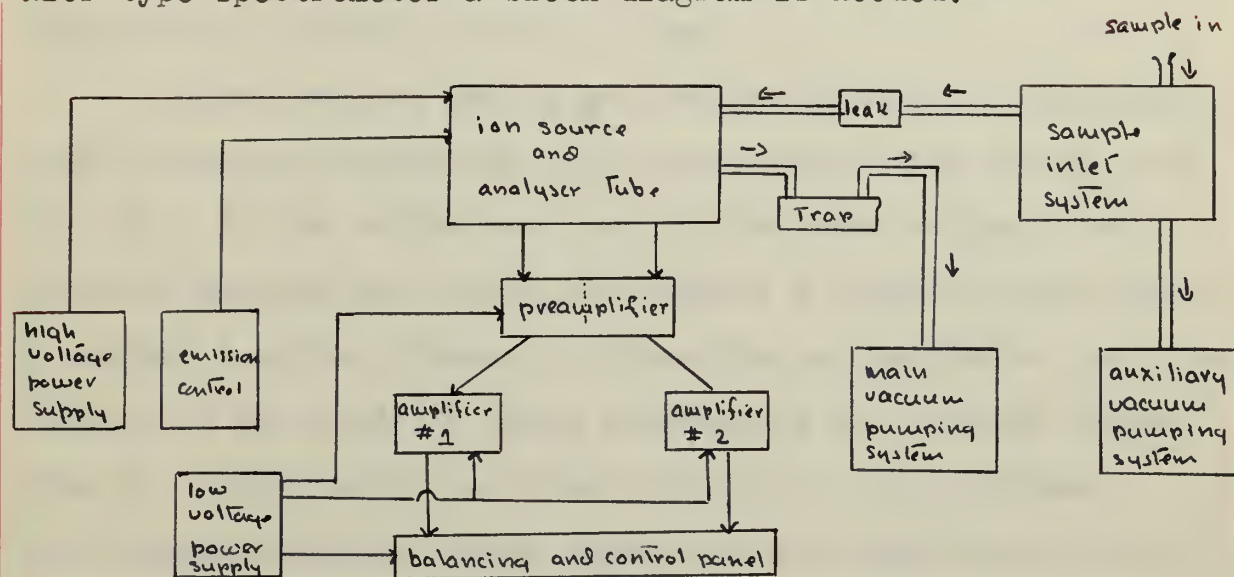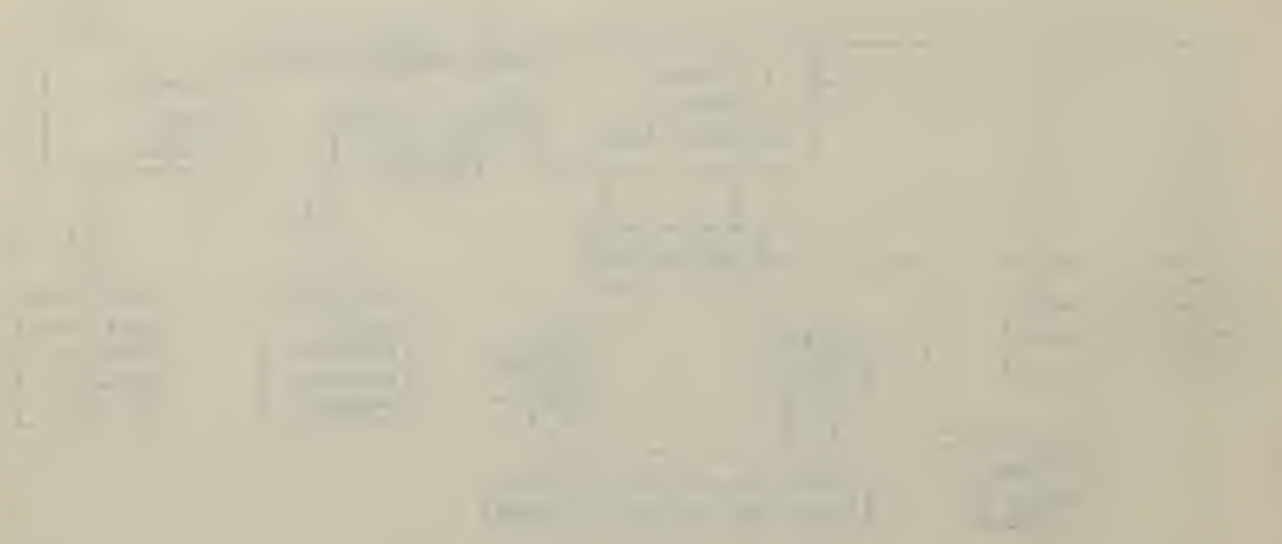Nier-type spectrometer a block diagram is needed:

Fig. 1. A block diagram of the Nier-type
spectrometer

Starting with the "sample intake" the sample was ad-
mitted into an evacuated system, which was kept at a pressure
of 10^{-6} mm Hg, by lowering a column of mercury by means of a
Toeppler pump. Once the stopcock of the sample bulb was closed
the sample could be compressed by means of a column of mercury
to give the desired leak pressure. The sample was, in this

way, forced through a long capillary leak. The rate of flow through the leak was a fraction of a centimeter per hour. It was possible, by compressing the capillary leak with a brass block, to further reduce the flow. When the sample had been analyzed a sufficient number of times it was pumped out through the auxiliary pumping system.

After the gas sample had passed through the capillary leak it passed through the gas inlet into the ion source (see Fig. 6). In the source the various electrode voltages were admitted through the top of the tube by a glass to metal seal. A slender tungsten filament ionized the gas molecules, and once ionized in the space of three centimeters the voltage dropped from up to 2000 volts to ground potential -- in this way accelerating the ion. Also present in the source were several focussing electrodes which focussed the beam more precisely through the narrow slits.

The accelerated ions were shot down towards the variable magnetic field and since the particles were charged they were deflected by the field. The separation of the particles depended on the difference in the masses, in this way, as the accelerating voltage was varied, one mass at a time passed through the narrow slit in the preamplifier collecting plate (see Fig. 7).

Inspection of the ion collector assembly shows that the slit connected to the #2 collector is extremely narrow, in effect permitting passage of only one mass at a time. The #1

collector was much larger and could accommodate several masses
in the range where they fell close together. It was possible
with nitrogen, oxygen and CO_2 (the important biological
elements) to have the heavy isotope, which was the less in-
tense, pass through the slit in collector #1 and strike
collector #2. The main isotope fell on #1 and simultaneous
measurement was possible.[1] With hydrogen simultaneous measure-
ment was not possible, and a different method had to be used
(as explained in the section on spectra).

The small ion current striking the collector plate was
amplified in the preamplifier and the D.C. amplifier, and the
output was put on the balancing network.

Voltages for the electromagnet and D.C. feedback
amplifiers were provided by regulated power supplies. The out-
put voltage for the electromagnet was 175 volts and for the
amplifiers was 225 volts. In the amplifier circuit was a time
delay circuit to prevent excess output current during the
warming up period. The stability of the power supply circuits
was such that a change in line voltage of 5 volts on either
side of 115 volts produce a change in output voltage of
approximately one part in 5000.[2]

The other circuits consisted of a high voltage power
supply which provided the 2000 volts for ion acceleration and

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[1]Nier, Alfred O. "A Mass Spectrometer for Isotope and
Gas Analysis" The Review of Scientific Instruments, June 1947,
Volume 18, No. 6, p. 401.

[2]Ibid., p. 402.

for the Phillip's gauge. There was a voltage divider which
tapped off each step of ten volts and a rheostat which covered
the intervening portion. The stability for this circuit was
approximately the same as for the power supplier.

Finally there was an electron emission regulator which
regulated the total electron current leaving the filament. The
entire circuit was well insulated, as it operated at 2000
volts above ground.[1] It supplied regulated voltages to the
shield and trap and filament.

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[1] *Ibid.*

III. VACUUM TECHNIQUE AND LEAK HUNTING

The part of the system that gave us the most trouble during construction was the vacuum system. The following section describes some of the difficulties which were experienced, and the methods developed for correcting them.

Types of joints and methods of correcting leaks in them.

There were three types of joints in the vacuum system, and it was found, in general, that the leaks would occur at the joints rather than anywhere else. The joints were: glass to glass, glass to metal, or metal to metal.

The glass to glass joints were the easiest type in which to locate a leak and correct it. They were found by using a leak tester and corrected by heating and blowing. A bad crack in the glass system generally turned out to be a more expensive affair to fix than a fault in the metal system, as a professional glass blower was employed to do the work.

The metal to glass seals gave remarkably little trouble. There were only two of them -- in the intake system -- the joint from the system to the oil distillation pump and the joint from the thin capillary leak on the intake of the spectrometer tube to the glass system. In both cases the method was the same. Both the glass and the metal were heated with a capillary flame and hot wax (pycein) dropped on

the seal. The wax was warmed with the edge of the flame until it ran smooth. After several hours a coat of glyptal was applied. The next day another coat of glyptal was applied. In the case of a small leak this was done with the vacuum pumps on, as it is advisable for some of the wax to be sucked in. On large leaks there was atmospheric pressure on both sides of the leak, as too much wax might be sucked through. By experience it was found better to take the time to make a very tight fit between the glass and metal, or use an adaptor if necessary, as there was trouble with wax getting into the system and condensing on the gun.

The metal to metal seals gave by far the most trouble. There were two types, flanges which were bolted together (this type connected the cold trap to the rest of the system), and hard-soldered joints, by which the spectrometer tube was held together. The flanges were made of steel, as it was discovered that brass warped quite easily, and had eight holes through which the large bolts were placed. After much experimenting with hard and soft rubber of varying thicknesses for gasket material Teflan was used -- a rugged, acid-resistant plastic made by DuPont. The flanges were bolted with heavy steel bolts and were tightened with a long wrench with a foot of pipe on the end of it.

The spectrometer tube itself was soldered together with hard solder. Occasionally, while outgassing, a leak was sprung in the hard solder. A small leak could be corrected by

painting with glyptal, baking for several hours with a lamp,
then adding another layer and baking again, etc., until the
leak was fixed. With this technique, however, there was always
the possibility of introducing a virtual leak into the system,
i.e., an air pocket which could not be pumped out for days.
Once or twice it was necessary to hard-solder the joint because
of large leaks. This was a ticklish business, as it was easy
to open up new leaks during the process. It also took a long
time as there was no way of testing the tube except by putting
it back in position, and the soldering had to be done on the
bench. It was found that the solder ran best on the monel
metal, using hydrochloric acid flux.

Vacuum measuring devices

In the large system there were three types of vacuum
measuring devices. There were two thermocouple gauges. The
thermocouple gauge operated from atmospheric pressure to 10^{-4}
millimeters of mercury. After this value it was fairly in-
sensitive. A thermocouple gauge was used between the mercury
distillation pump and the forepump to be sure that the mercury
pump had enough backing pressure to operate. A backing
pressure of around 10^{-3} mm Hg was satisfactory. There was very
little trouble with this part of the system, and a rise in the
backing pressure could usually be attributed to dirty oil in
the pump; so the single gauge was sufficient. The second ther-
mocouple gauge was placed in the trap above the valve so that

the valve could be closed and the rate of leak of the spectrometer tube measured (see below).

A VG 1A ionization gauge was put right above the thermocouple gauge. This gauge measured from 10^{-4} to 10^{-7} mm Hg. The vacuum was supposed to stay around 2×10^{-6} mm Hg. Above 10^{-5} mm Hg the tungsten filament in the spectrometer would burn out. Above 10^{-4} mm Hg the filament in the ion gauge would burn out. There was a relay connected to the Phillips gauge to turn off the tube filament when the pressure rose, but there was nothing to save the ion gauge in the event of a sudden leak or carelessness, and consequently many gauges were burned out. These could be changed without delay, however, as several of them were kept on hand with electrical connection made. The procedure was to close the valve (thereby holding the vacuum in the trap), unscrew the cap which held the brass ring and rubber gasket in place (see diagram), regrease the gasket with a vaporless grease, fit the gasket to the new VG 1A, screw it in place again, and open the valve. If this was properly performed, the vacuum was back about fifteen minutes after the ion gauge burned out. The new ion gauges had to be outgassed carefully. The filament was outgassed by increasing the current through it which could be done by means of the electronic circuit. The plate and envelope could be outgassed with a capillary flame, and the grid was outgassed by passing 7 amps through it for ten minutes or so.
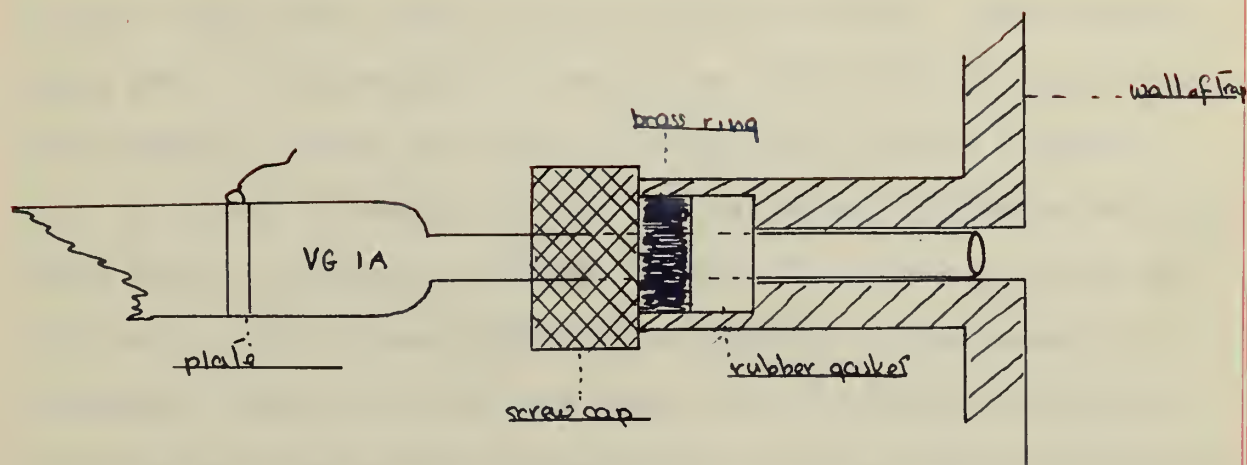
Fig. 2.   VG 1A Ionization Gauge

It was originally intended to rely solely on the
Phillips gauge which was part of the spectrometer tube and
operated the relay which cut off the filament when the pressure
rose.   The ion gauge and thermocouple were to be used during
construction and for test purposes only, as they required two
extra chassis for their circuits, and also the Phillips gauge
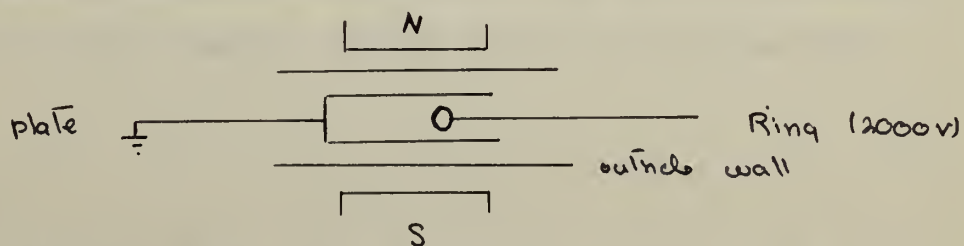had the range of the two combined.   The inside of the
Phillips gauge looked like this:

Fig. 3.   The inside of the Phillips Gauge

Calibration of the Phillips gauge with the known ion gauge was attempted very early during construction, but it was immediately noticed that there were certain discontinuities. The Phillips gauge meter would remain at one value while the ion gauge meter fell steadily, then the Phillips gauge meter would suddenly drop ten scale divisions or so. It was finally discovered that there was an intermittent short between the plate and the outside wall, and on investigating the inside of the gauge it was determined that the plate had been made of nickel, instead of a non-magnetic material as specified, and was being magnetized and pulled against the outside wall by the strong permanent magnet. It was around this time that the old vacuum trap was recognized to be unsatisfactory and the new one was designed. A much wider opening to the ion gauge was included, as it was thought that possibly the opening had been too small and too far away from the Phillips gauge to give good results. After these changes the Phillips gauge proved to be more dependable, although never as accurate as the ion gauge. However, as it was only necessary that the vacuum be of the order of 10^{-6} mm Hg, this was in general satisfactory, and the ion gauge was retained for cases where a higher degree of accuracy was necessary.

Outgassing

When work on the vacuum system was started, the outgassing was taken rather casually; but it was soon learned,

through trial and error, that in order to achieve the last factor
of ten in the vacuum it was necessary to outgas thoroughly
and systematically. This conclusion was only arrived at after
the second trap had been installed. Outgassing this trap by
heating iy for ten or fifteen minutes with two hand torches
was attempted. The pressure went so high that it was evident
that a great deal of foreign matter was being driven off, even
though the trap had been thoroughly rinsed with acetone and
alcohol before installing. It was then decided to heat the
trap electrically. 220° C. was arbitrarily set as the tempera-
ture at which it was to be outgassed, and by determining the
mass of the trap (from its specifications) and knowing its
thermal capacity it could be calculated that 10^6 Joules were
needed to heat the trap. By knowing the number of ohms per
foot of the resistance wire, the number of feet needed to bring
the trap to this temperature could be determined. The trap
was then wound with wet asbestos tape and the wire embedded
in it while it was still damp (care being taken that none of
the wire was in contact with the metal of the trap). Then
the resistance wire was covered with more asbestos tape, which
hardened nicely when dry. The same technique was used on the
spectrometer tube, with care to avoid heating the ion source,
the hard-soldered joints, or the Phillips gauge. These were
always done with a hand torch.

The method in general was to outgas the spectrometer
tube thoroughly with the trap cold, and, after turning off the

heating coils, to allow the vacuum to come to a stable value. The valve was then closed and the trap heated for half an hour or so. In this way the foreign matter was driven into the trap by the first outgassing and carried down into the pumps by the second. Occasionally the cold trap was siphoned out and boiling water poured in to free the walls of matter which had condensed on them. This treatment, though tedious, paid off after several weeks. The outgassing was usually done the last thing before leaving in the evening. The trap was filled with dry ice and acetone. By morning almost all but a few small pieces of dry ice would have melted. The acetone was siphoned out and the trap filled with liquid air, and the ion gauge was outgassed.

The intake system was outgassed relatively easily with a hand torch.

Leak-hunting

From time to time it was found that, due to continued pumping on a weak spot, vibration, strains, or some other cause, a leak had been sprung. In the intake system this was easily located by means of the leak tester or by cleaning the stopcocks with acetone and regreasing them. In the large system the problem was more difficult. The bolted joints were always suspect first. These were sprayed with acetone, the ion gauge meter being carefully observed. A rise in pressure would indicate that some of the acetone had got into the system. The reaction time was very fast indeed. This was an

excellent method where a very large leak was concerned -- i.e., when the vacuum had risen to the order of 10^{-3} - 10^{-4} mm Hg. For small leaks, when the vacuum remained at 10^{-5} or better, the spectrometer could be turned on and the instrument itself used as a leak tester. Using helium or natural gas, the spectrometer would be set on the helium or methane peak, and a sharp rise in amplitude could be observed as parts of the tube were sprayed with the gas.

Another method which was of use in an ailing vacuum system was a rate-of-leak measurement. This helped to determine in which part of the system the leak was located. The volume of the cold trap and the spectrometer tube were known (considered separately, as they could be isolated by means of the valve). In order to determine the rate of leak for the mass spectrometer tube, the valve was closed, and, using the thermocouple gauge, the time for it to change was obtained by an arbitrary number of scale divisions. (It was necessary to use the thermocouple gauge with all but the very best vacuum as the ion gauge would go off scale during the measurement). Knowing the initial and final pressure and the time elapsed, the expression for "rate of leak" was

$$\frac{V_{total} (P_f - P_i) \times 3600}{t}$$ micron cubic feet per hour. By

remembering to do this when the vacuum was good, the values could be compared, and it proved a good technique with many stubborn leaks.

A virtual leak could be discovered in this manner. There was considerable trouble with the new trap when it was first installed, and it was discovered, after much difficulty, that the valve had been packed with asbestos. The asbestos had absorbed the acetone when the trap was washed and the acetone was evaporating and causing considerable vapor pressure.

Some conclusions about vacuum systems

After many months of difficulties with the vacuum systems, a few general conclusions could be drawn:

The metal system was the harder of the two in which to locate leaks, but was, on the whole, easier and less expensive to repair than the glass system.

It was most fortunate that there was a mercury pump rather than an oil pump in this system, as the mercury pump could be opened to atmosphere without a wait until it cooled off, whereas the oil would oxidize.

It was convenient to have a number of vacuum measuring devices in various parts of the system as they helped locate a difficulty quickly, although they were more trouble to provide for originally.

It was of great value to be able to take the system apart quickly (by means of the flanges).

The relays were important (there was a water relay which turned the pumps off when the water failed) and saved

many filaments and a great deal of trouble from vaporized
mercury.

Teflon is an excellent gasket material.

Outgassing is very important.

And finally, it must be said that a vacuum system re-
quires long acquaintance with its own particular symptoms and
a wealth of recorded observations before it can be relied upon.

IV. SPECTRA

Variables in operation

As soon as the vacuum system had been completed, mass spectra were run on the air that remained in the tube. These spectra covered the whole range from mass one to mass two hundred, and were done one the narrow slit amplifier which admitted one mass only at a time. The range was covered by keeping the magnetic field constant around 3000 or 4000 gauss and by varying the accelerating voltage from zero to 2000 volts. The mass at any particular voltage setting was determined from the equation $H^2 = \dfrac{MV}{4.82 \times 10^{-3} r^2 e}$ where H was the magnetic field in kilogauss, V was the accelerating voltage in kilovolts, M was the mass of the isotope, r was the radius of the magnetic field, e was the charge on the electron, and the constant was a constant of the instrument. In a typical air sample the main peaks present were oxygen 32, the nitrogen isotopes 28 and 29, carbon dioxide 44, 45, and 46, the H_2O peak, and a carbon monoxide peak at mass 28 which was superimposed on the largest nitrogen peak. The 28 peak was by far the largest and was used to calibrate the instrument whenever the results appeared to be slightly off due to the hysteresis of the magnet.

For all samples during the first few months of running

the following values were recorded:

Trap Current. The trap-shield ratio was maximized by
focussing the magnet on the gun so that the greatest possible
number of electrons were focussed into the trap and were not
scattered into the shield. Dr. Nier's ratio was 0.015, the
Harvard spectrometer's was 0.02. The trap current was then
maximized (the ratio remaining the same) by a rheostat in the
emission regulator chassis. This gave the greatest possible
ionization of the sample.

Emission Voltage. This voltage did not affect the
ratio of two isotopes, but gave a greater amplitude to the
single peaks in the event of a small sample or an isotope that
was relatively scarce like hydrogen 4.

Focus. This factor did not seem to affect the peaks
in any consistent fashion. The focus was adjusted to give
maximum peak height and minimum peak width.

Pressure. The pressure within the system made a great
difference in the accuracy as a high background increased the
isotope by a greater percentage than the main peak. For a
main peak ot ten volts a background of three to four millivolts
was permissible. Backgrounds were recorded before and after
each run and the average background was subtracted from the
main peak height before calculating the ratio.

Leak Pressure. Too low a leak pressure meant that the
peak height was unable to overcome the effect of the background
and too high a peak pressure would give an amplitude which was

off scale for the main peak. The general magnitude of the leak pressure was of the order of several tenths of a cubic centimeter per hour.

Nitrogen and CO_2

After running on air samples under various conditions for several weeks in order to identify the characteristic peaks for calibration purposes, samples of tank nitrogen and CO_2 were run. It was found using nitrogen that there were unexplained peaks at masses 27.0, 26.0, and 25.0. For an amplitude of ten volts for the N_{28} peak and 60 millivolts for the N_{28} peak the other peaks would be 50, 30, and 10 millivolts as shown below:
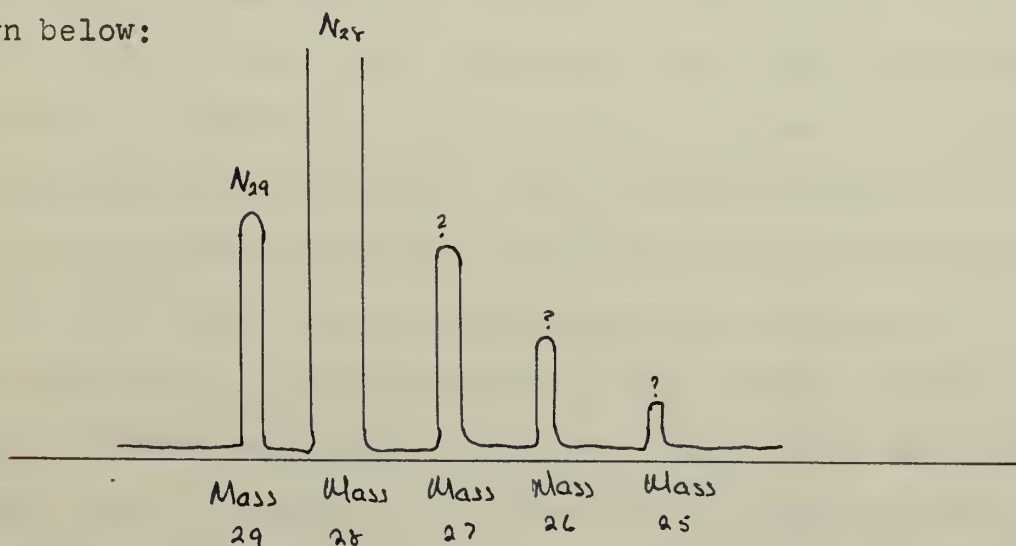
Fig. 4. A typical nitrogen spectrum

These were not nitrogen isotopes and this difficulty was reported by Dr. Nier also. They could be lessened in ampli-

tude somewhat by refocussing, but were always evident to some extent, and to the author's knowledge have not yet been explained. The ratios obtained for nitrogen varied from $N_{29}/N_{28} = 1/135$ to $N_{29}/N_{28} = 1/87$, the proper value being 1/120. The CO_2 region was investigated around the same time, various small changes being made as the data accumulated.

It was discovered during these preliminary runs that the double feedback amplifiers were considerably more sensitive to outside stimuli than had originally been expected. They were found to require at least two hours in the morning to warm up after being turned on. Several new relays were installed and the amplifiers were left on all night. This saved many hours of running time. The amplifiers were also extremely sensitive to vibrations in the room, and it was found advisable to mount both the preamplifier and the backing pumps (which caused considerable vibration) on sponge rubber 3/4" thick. During humid summer weather the amplifiers were apt to be less stable than usual, and evacuation of the preamplifier was considered. Technically this would have caused many difficulties, however, and so the case was fitted with a tight gasket, the one aperture stopped with a tight rubber stopper, and two petri dishes of silica gel were kept inside it all the time. Using these precautions and barring minor mishaps the amplifiers fluctuated not more than one millivolt.

Hydrogen

After these difficulties had been resolved the CO_2 region became considerably more reproducible, and although there was more work to be done to bring the instrument to an accuracy of four or five decimal places, it was considered necessary to commence the hydrogen runs, as that was the use for which the spectrometer was intended. The hydrogen peaks of mass one and two (H^+ and H_2^+ D^+) were relatively abundant and were easy to locate by setting the magnetic field down to 100 gauss and scanning the spectrum from 2000 volts down. Masses three ($H\ D_2^+$, and HHH^+) and four (DD^+) in normal hydrogen were exceedingly hard to find, and it was necessary to turn the emission up high and also to realign the whole spectrometer tube in its seat so that the electrons would surely travel perpendicular to the magnetic field and land on the collector plates.

In the case of hydrogen runs it was possible to use either amplifier, as the peaks were so far apart that it was impossible to have two of them fall on the wide collector plate at the same time. This was an advantage, as one amplifier was often more stable than the other. It was also found convenient in the case of hydrogen to use a magnet scan rather than a voltage scan, as a large difference in accelerating voltage between the location of the peaks frequently affected their amplitude, the higher accelerating voltage producing the

larger peaks. The voltage, then, was maintained at a high value (around 1800 volts) to give maximum amplitude, and the magnetic field was varied from zero to several hundred gauss. The magnetic field variation did not need to be particularly great as the mass was proportional to its square, rather than the first power, as in the case of the voltage.

Since the current through the magnet was so small, and since it was varied often, due to the use of a magnet scan, any hysteresis was apt to be more troublesome than in the case of the previously discussed elements. It was necessary to re-zero the magnet at least once a day. This was done by reversing the current through coils (by means of two pin jacks). A small iron needle was suspended on a thread between the pole pieces. The rheostat controlling the current was turned up until the needle was no longer attracted by the magnet. This gave the zero position. The pin jacks were then pulled and the rheostat set at zero.

When the instrument was running smoothly and reproducivly on the hydrogen samples, enriched samples were introduced. The method, which had been outlined by Dr. Nier, on the enriched deuterium samples was as follows:

The leak pressure was varied, by means of the Toeppler pump, from a gauge reading of one centimeter to a gauge reading of nine centimeters. Readings of masses two and three were taken at four or five different leak pressures within that range, with a constant voltage and varying magnet. The

3/2 ratio was then calibrated and this was plotted against the mass two amplitude at each point. The mass two amplitude was roughly proportional to the leak pressure. From this the intercept on the 3/2 ratio axis, where mass two had theoretically zero amplitude, was read off. This intercept gave the HD^+/H_2^+ value. The intercept was read because the slight rise in the curve at higher leak pressures was due to HHH^+ ions which gave the mass three peak a greater value. The HD^+/H_2^+ value obtained from the intercept had to be corrected by a constant factor for the molecular flow effect, as the two masses were not pumped through the system at the same rate. Mass two went through faster than mass three, and an uncorrected ratio would have had a higher value. The D/H or %D in the sample was then determined by dividing the HD/H_2 corrected value in half.

The percentages were found to be accurate to three decimal places on the same sample. However if the percentage was varied on the next sample it took several runs to clean the system of the previous sample. Several runs were taken on each sample to insure accuracy.

V. CONCLUSION

The instrument which has been described on these pages did not come up to the standards of reproducibility and precision which were expected of it. Dr. Nier states of his instrument that the mean duration from the average of 1.005 in the ratio of the CO_2 isotopes was 0.003.[1] During the author's period of work the Harvard instrument never gave a better result than a mean duration of 0.17 from the average of 0.99 on the 3/2 hydrogen ratio. This is extremely poor, especially as the most careful work was done in the hydrogen region.

It is probable that the construction of this particular instrument was at fault, rather than the design. The design has been taken over by Consolidated who produce it with photographic recording, automatic scanning, and high resolving power.

The many small improvements which Consolidated has made on the design make it possible for a sample to be analyzed very rapidly. This factor makes the instrument extremely useful in studying the combustion of fuels at various stages. It is useful in the petroleum industry for examination of the many hydrocarbon present in the samples. It is important in isotope tracer work, both in commercial fields and in the

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[1] Ibid., p. 409.

biological sciences.

This latter application is probably the most interesting to the "pure" scientist. It is possible by mass spectrometer analysis to show the exact position of the heavy isotope in the molecule, thus indicating the manner in which the molecules undergo rearrangement and conversion.[1] It is possible also to observe lifes most vital processes in the living organism and analyse the components necessary to its well being. These contributions alone are enough to make the instrument necessary and important.

[1]Consolidated mass spectrometer model 21-102.

VI. SUMMARY

In recent years one of the most important applications of physics to the biological sciences has been the tracer method. The detection and measurement of the abundance of stable isotopes used in tracer work is done by a mass spectrometer. Several types of mass spectrometers have been designed, the most recent being the Nier spectrometer. This particular instrument is now being manufactured commercially. The instrument which is described by this thesis is a Nier spectrometer which was constructed for use in tracer work at the Harvard Medical School before they were available commercially.

The instrument is described briefly: the sample is admitted with an evacuated system and passes through a capillary leak into the ion source. Here the molecules are ionized and accelerated by a 2000 volt potential. The ions pass through a magnetic field in which they are deflected according to their mass. The ions pass into the collector assembly and the tiny ion current is amplified by a preamplifier and a D.C. amplifier. This current goes into a measuring circuit which gives the abundance ratio of the isotopes. The voltages are supplied by regulated power supplier to the electromagnet, the amplifiers, and the ion source. The emission current is controlled by an emission regulator.

Many difficulties were experienced in the construction of the vacuum system. The difficulties and their correction are described in detail.

There were three types of joints in the system: glass to glass, glass to metal, and metal to metal. The methods of joining, symptoms of trouble, and ways of dealing with leaks are considered in each case.

Three types of vacuum measuring devices were used: the thermocouple gauge, the VG 1A ionization gauge, and the Phillip's gauge. The advantages of each, the ranges, and physical location of each are discussed.

The importance of outgassing is evaluated and techniques for doing so in various parts of the system are mentioned.

Different methods of locating leaks are described, including spraying with acetone, using a glass leak tester, and using the mass spectrometer itself are described. The usefulness of a "rate of leak" measurement is stressed.

Some conclusions on vacuum systems in general are drawn from the experience with the particular one described.

The mass spectra which were run after completion of the vacuum system are described. The variables of the instrument such as trap current and emission voltage are discussed.

Various difficulties which arose during the first weeks of running, such as instability in the amplifier are mentioned, as are the steps taken to correct them.

The methods and difficulties encountered in making hydrogen run are described. The differences between operation and calculations of this element and the heavier ones are explained.

Some of the data on reproducibility is given. A few of the uses are mentioned, in particular the importance of the instrument to the biological sciences is stressed.
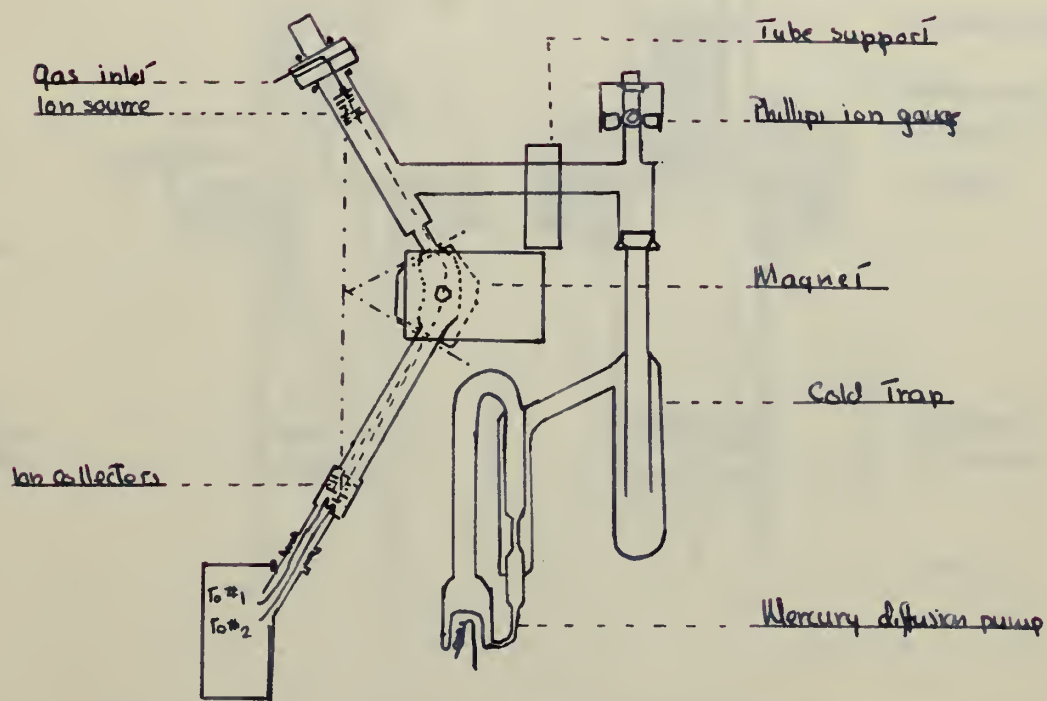
Fig. 5   Schematic drawing showing mass spectrometer Tube, magnet, pressure gauge, and pumping system.

gas inlet

glass Tubing

Shield S
Focus plates J_3
ground plates

J_2
D

8 Wire press seals

Water cooling tube
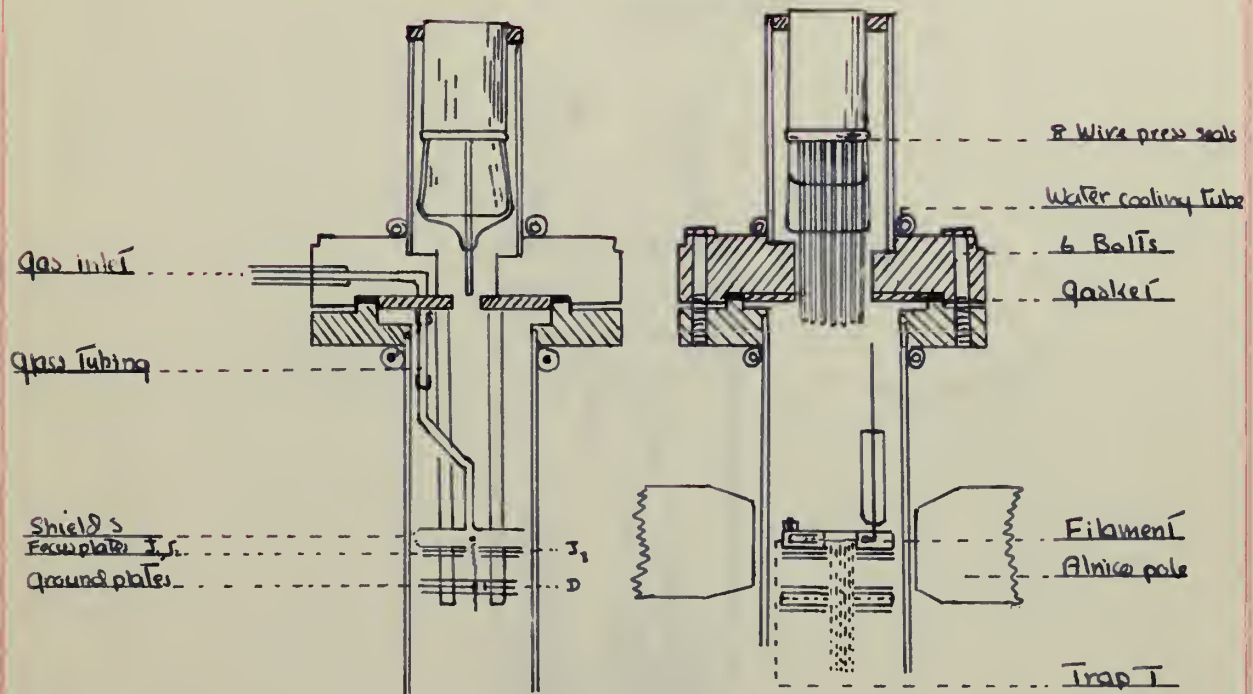
6 Bolts

Gasket

Filament

Alnico pole

Trap T

Fig 6. Ion Source. Filament made of Tungsten ribbon, 0.75 mm wide and 0.025 mm Thick. Electron beam defining slit 0.5 × 20 mm Thick. All plates are made of Nichrome V 0.025" Thick. J_1, J_2, and J_3 are focus plates. G_1, G_2, and G_3 are ground plates. A voltage on D pulls The beam off The collector plates.
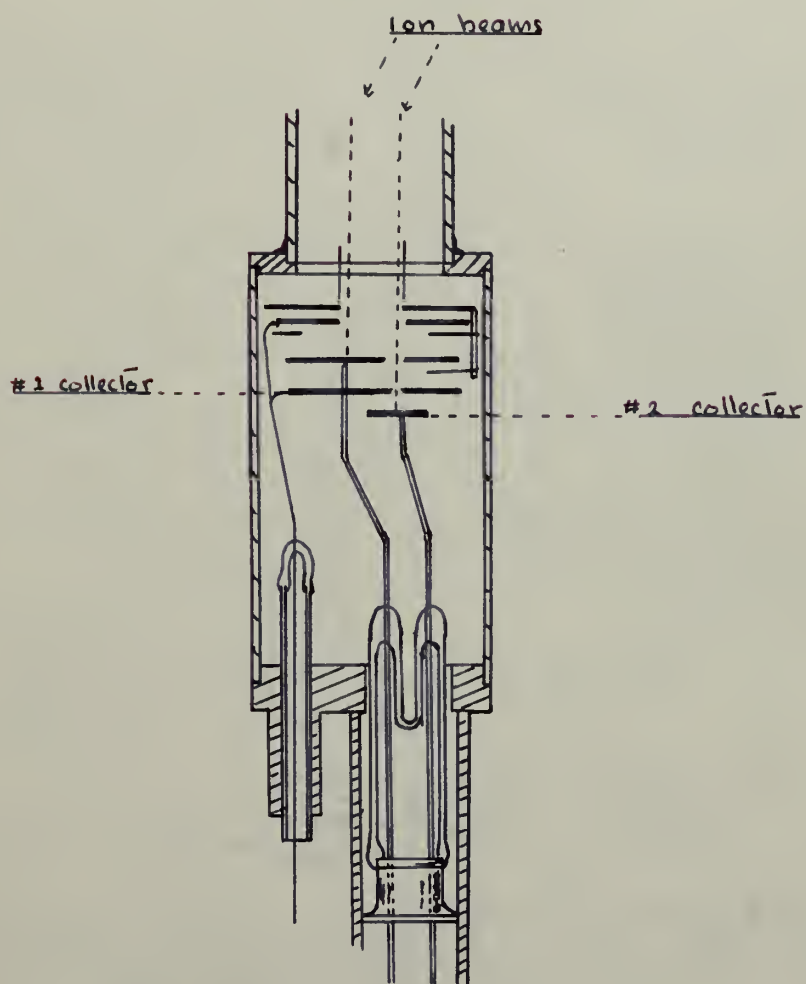
From Nier, Alfred O. Ibid

Fig 7. Ion collector assembly. Extra plates in collector assembly suppress secondary electrons emitted by ion bombardment, and prevent ground current leakage.
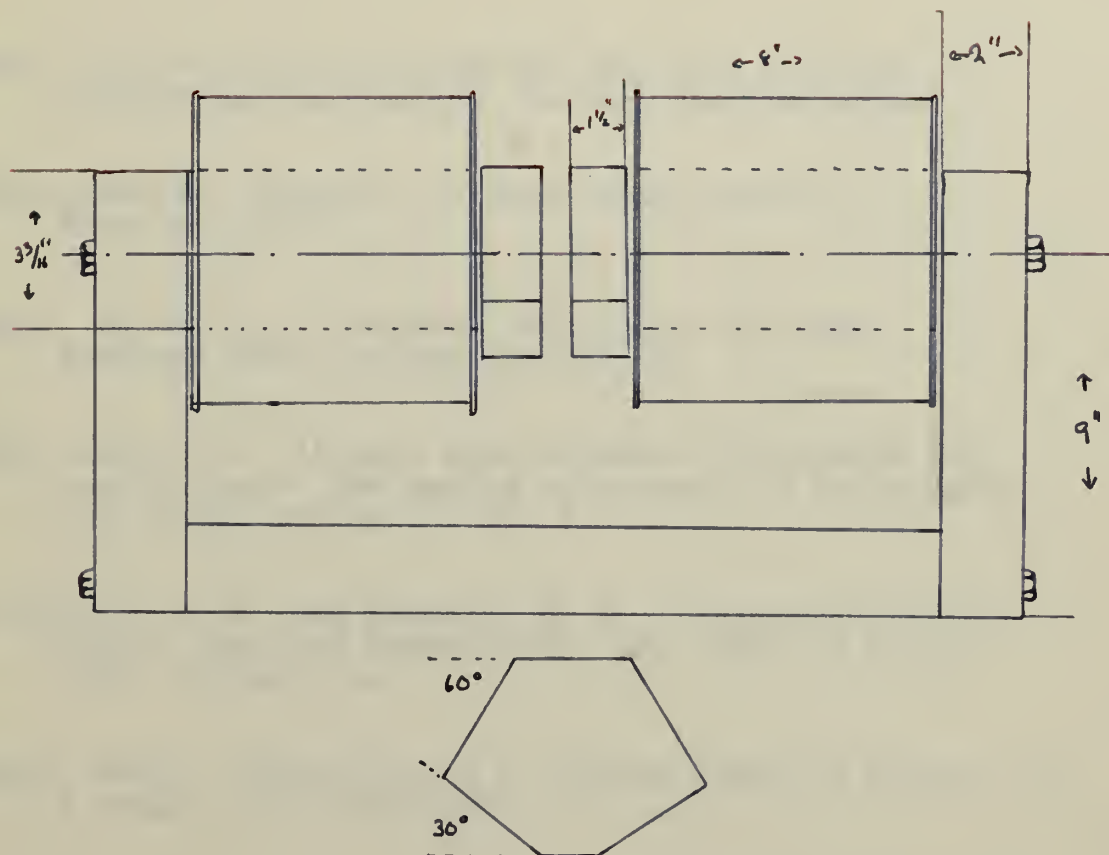
From: Nier, Alfred O. Ibid

Fig 8. Cross sectional view of electromagnet. When connected in series
The magnet coils have a resistance of 1600 ohms, and a current
of 90 ma produces a field of 2800 gauss, sufficient for collecting
CO_2 ions having an energy of 2000 volts.

From: Nier, Alfred O.
                Ibid

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